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Transport of Dissolved Organics from Dilute Aqueous Solutions through Flexible Membrane Liners

Matrecon, Inc., Alameda, CA

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Transport of Dissolved Organics from Dilute Aqueous Solutions through Flexible Membrane Liners

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ABSTRACT

This paper presents the results of experiments relating to the partitioning of dissolved organics from dilute aqueous solutions to polymeric flexible membrane liners (FMLs) and their permeation through these liners. In order to simulate partitioning and the transport of waste constituents within and out of a landfill, two sets of experiments were performed. In the first set, samples of an FML that were either unexposed or saturated with an organic were placed in test liquids, including deionized (DI) water, neat organics, and saturated aqueous solutions of organics. In the second set, the partitioning of organics in aqueous solutions to water and air on the other side of FML barriers was measured in a three-compartment closed apparatus. The results of these experiments show that, even at low concentrations in an aqueous solution, some organics can be highly absorbed by a polyethylene (PE) FML, reaching equilibrium concentrations in less than 120 hours. Trichloroethylene (TCE), toluene, and o-xylene migrated from the dilute aqueous solution and penetrated a PE FML and were detected in the airspace above the air and water below the FML barriers in as short a time as 24 hurs after the experiment had begun.

INTRODUCTION

Even though of FMLs are recognized for their low permeability to water and waste liquids, their permeability to gases, vapors, and liquids can vary by orders of magnitude (1, 2, 3, 4, 5). The amount and rate at which a constituent of a waste liquid can migrate through an FML and the direction of migration depend on characteristics of the consitituent (e.g. the solubility parameters of the constituent with respect to those of the FML), the FML (e.g. crystallinity content of the polymer), the temperature, and the concentration of the constituent on both sides of the FML. Since polymeric FMLs are nonporous materials, constituents permeate them by a three-step process that involves the solution or absorption of the permeant at the surface of the FML, transport of the permeant through the membrane by diffusion, and evaporation or desorption of the permeant on the downstream side. As a first approximation, the magnitude and

the difference in concentration of an individual species across a membrane determine the direction and the driving force for the permeation of that species. Individual organics can permeate an FML at substantially different rates. In a lined waste disposal unit, an FML generally encounters dilute solutions containing both organic and inorganic species. The individual species may interact with one another and with the FML in different ways, possibly having a significant effect on the permeation rates of the organic species through the membrane.

PARTITIONING

The distribution of a dissolved substance between two phases that are essentially immiscible has been an important subject for study in chemistry for more than a century (6). Some of the early investigations showed that at equilibrium the ratio of the concentrations of a substance dissolved in two immiscible solvents in contact with one another is constant and does not depend upon the relative volumes of the solutions involved. Later studies showed that the distribution would be constant only if a single molecular species was being considered as being distributed between the two phases, that is, the molecular species would be the same in both phases and would not either dissociate or associate when transferring from one phase to the other. Thus, the partitioning could be treated by classical thermodynamics as an equilibrium process and would be related to other commonly measured functions such as partial pressure, osmotic pressure, and chemical potential. The partitioning of a dissolved substance, for example, between water and an organic such as toluene, forms the basis for the separation of organic compounds by extraction. When there are two or more immiscible phases, an organic solute, for example, will partition or distribute itself among phases depending upon its solubility in the different phases. Many organic solutes will tend to be more soluble in the organic phase and remain in that phase unless the solute is exceptionally soluble in water. Nevertheless, a small amount of the organic will dissolve in water when the two phases are in contact. The ratio at which a solute partitions between the organic and aqueous phases is termed the partitioning or the distribution coefficient and is determined by dividing the concentration of the dissolved substance in the organic phase by its concentration in the aqueous phase.

The concept of partitioning is being used in tracking pollutants and contaminants in the environment, e.g. pesticides and various organics which resist biodegradation, including the polychlorinated biphenyls (PCBs) (7, 8). These chemical species can move through the food chain, resulting in higher concentrations at each trophic level. This process which reflects the greater solubility of an organic chemical in oily tissue than in water has been termed "bioconcentration." The process of partitioning is also involved in spill cleanup processes in which polymeric materials are used to absorb a spilled organic.

In waste containment, a similar situation exists with respect to polymeric FMLs and waste liquids that contain dissolved organic substances. Organics dissolved in waste liquids can partition between the waste liquid and the liner and thus enter and swell the liner causing changes in other properties. The organic can then permeate and be transported through the liner at a rate which depends on the chemical properties of the liner, its thickness, the temperature, and the concentration gradient, or more precisely, its "chemical potential" gradient across the liner. Inasmuch as FMLs are organic compounds and are at least partially amorphous, they can behave much like liquids from a thermodynamic standpoint.

The major chemical properties of an FML that affect the magnitude of its swelling in a liquid include:

- the solubility parameters of the polymer with respect to those of constituents of the liquid,
- the degree of crosslinking of the polymer,
- the crystallinity content of the polymer,
- the filler content of the FML compound,
- the plasticizer content of the FML compound, and
- the soluble constituents of the FML compound.

Due to differences in polymers and in compounding, the importance and applicability of these properties vary from one FML to another.

For rubber and noncrystalline or amorphous polymers, the solubility parameter is probably the most important property affecting the magnitude of swelling and can be used by polymer scientists to measure the compatibility of an amorphous polymeric composition with a liquid with which it may be in contact.

Crosslinking of a noncrystalline polymer or a rubber reduces its ability to swell in a liquid which has similar solubility characteristics to the polymer. The amount that a crosslinked polymer swells in a good solvent for the raw polymer can be used to measure the degree of crosslinking: the less the swelling, the greater the crosslinking.

Crystallinity of a polymer acts much like crosslinking to restrict the ability of a polymer to swell and dissolve. The crystalline domains of a polymer do not absorb organics. Highly crystalline polymers, such as high-density polyethylene (HDPE), will swell slightly but will not dissolve in gasoline even though they are both hydrocarbons.

The ingredients that have been added to an FML compound to impart specific properties (e.g. aging or processing characteristics) and their concentration in the manufactured FML can also affect the magnitude of swelling of noncrystalline polymeric compositions. As with the crystalline domains in semicrystalline polymers, nonporous particulate fillers, such as carbon black, silica, or clay, do not absorb organics. Plasticizers are generally extractable by organic solvents, but most are only slightly extractable by water.

Rubber and plastic compounds may contain minor amounts of water-soluble inorganic salts which enter the compound via the polymer itself, e.g. catalyst traces, salt used in flocculation, etc., and via small amounts in the various compounding ingredients, e.g. many of the non-black fillers contain small amounts of water-soluble constituents. These water-soluble salts can cause swelling by diffusion of water into the mass by the driving force of osmosis.

In previous work, Haxo et al (9) observed that slightly soluble organics dissolved in an aqueous waste liquid can partition to an FML which is immersed in the liquid. That work included immersion of FML samples in dilute but saturated aqueous solutions of tri-n-butyl phosphate (TBP) at a concentration less than 1,000 mg L^{-1}. The time required to reach equilibrium, as determined by weight change, depended on the FML and, in some cases, equilibrium was reached only after several years. The amount of TBP absorbed at equilibrium also depended on the type of FML. It should be noted that TBP has a molecular weight of 266.3 and a relatively low volatility.

Immersion testing of the FMLs was also performed in neat TBP (10). In that experiment, the absorption of the TBP to equilibrium by various lining materials took place in a relatively short time and, in most cases, ended at considerably higher absorption values than the values in the tests with the saturated solutions, indicating an effect of concentration.

Because of the need for data on the partitioning of organic liquids in FMLs and on their transport through FMLs, this research was undertaken to determine the partitioning or distribution of selected organics between water and an FML, and the transport permeation of selected organics through an FML in a multicompartment apparatus that simulates the configuration of a waste landfill.

EXPERIMENTAL DETAILS

Two sets of experiments were performed for this study. In the first set, samples of an FML that were either unexposed or saturated with an organic were placed in test liquids, including deionized (DI) water, neat organics, and saturated aqueous solutions of organics. In the second set, the transport of organics in aqueous solutions through an FML was measured in a three-compartment closed apparatus. The concentration of the organics in each of the different test zones was monitored by gas chromatography (GC).

Gas Chromatography Procedures

A Perkin-Elmer Sigma Three Series gas chromatograph with a flame ionization detector was used for the GC analyses. The instrument was fitted with different columns as required to effect separation of the different mixtures of volatile and semivolatile organics. Different temperature programs for both the oven and the injection/detection ports were also used to maximize separation and response factors for the mixtures. The different conditions, injection volumes, carrier gas flow rates, etc., for each of the experiments are all presented in Table 1.

The concentrations of the organics in the aqueous solutions and the vapor zones of the test apparatus were determined by injecting samples removed from the aqueous and vapor zones directly into the GC column. The experimental apparatuses for exposing the FML samples featured septums through which the liquid and vapor zones could be sampled during the test to determine whether equilibrium had been reached.

The concentrations of the organics in the FML samples were determined either by the change in weight of the FML samples or by headspace gas chromatography (HSGC). In the HSGC procedure, an exposed FML specimen is placed in a small vapor-tight can provided with a septum through which vapors from the specimen can be sampled. The can is placed in an oven at 105°C and heated for approximately an hour. A sample of the vapors is drawn from the can and injected into the GC. The FML specimen is removed from the sampled can and placed in a new can which is then heated in a 105°C oven for approximately an hour. Once again, the vapors inside the can are sampled and injected into the GC. The process of heating, sampling, and injecting is repeated until no organics are detected in the sampled vapors by the GC. The amount for each organic were summed to represent a total for the organic in the sample.

The concentrations of the organics in the injected samples were calculated by comparing peak height values resulting from the GC analyses with calibration curves. The calibration curves for the leachates were determined by injecting 1 μL of various solutions of known concentrations of the different organics into the GC column. Injections of each standard were performed five times to ensure reproducibility of injection techniques. Standard deviation was 2%. The calibration curves for the HSGC analyses were prepared by analyzing a specific volume of vapor (either 100 μL or 400 μL) from headspace cans injected with different volumes of a standard solution of organics.

Organics Used In Experiments

Selected chemical and physical characteristics of the organics used in these experiments is presented in Table 2. These organics were selected on the basis of their having been found in leachates and waste liquids and so that a range of solubility parameters and other properties (e.g. molecular weight, vapor pressure, and solubility in water) would be represented.

FMLs Used in Experiments

Selected property values of the linear low-density polyethylene (LLDPE) and the high-density polyethylene (HDPE) FMLs used in these experiments are presented in Table 3. These FMLs were selected because of their current use in waste containment applications and because neither would be dissolved by any of the selected solvents.

The property values were determined by the following procedures:

- volatiles in accordance with Matrecon Test Method 1 (5, 9),
- carbon black content by thermogravimetric analysis (5),
- density in accordfance with ASTM D792, and
- crystallinity content and melting point by differential scanning calorimetry (5).

It should be noted that the classification of polyethylenes based upon density and generally used by the polymer and plastics industry as set forth in ASTM

TABLE 1. CONDITIONS USED IN GAS CHROMATOGRAPHIC ANALYSES OF LIQUIDS AND VAPORS IN PARTITIONING/PERMEABILITY EXPERIMENTS

Set of conditions	Experiment	Column	Oven temperature program	Injection port and detector temperature (°C)	Injection volume (μL)	Carrier gas (He)[a] flow rate (mL $min.^{-1}$)	O_2/H_2[b] (psi)
1	Polyethylene specimens saturated with organics and placed in water	6 ft x 1/8 in. SS; 10% Carbowax 20M on 80/100 mesh Supelcoport	60°C for 1 min. to 140°C at 20°C/min.	250	Liquid: 1; Vapor: 400	30	40/30
2	Three-compartment apparatus with water spiked with TCE and toluene	DB WAX-1, 15M, polyethylene glycol, fused silica open tube (FSOT)	60° to 160°C at 20°C/min.	275	Liquid: 1; Vapor: 100	8	40/30
3	Three-compartment apparatus with water spiked with six organics	DB WAX-1, 15M, polyethylene glycol, fused silica open tube (FSOT)	60° to 160°C at 20°C/min.; 2 min. at 160°C	275	Liquid: 1; Vapor: 100	8	40/30

[a]Pre-purified helium passed through an oxygen trap.
[b]USP-grade oxygen used to burn the reagent-grade hydrogen in the flame-ionization detector.

TABLE 2. ORGANICS USED IN PARTITIONING/PERMEABILITY EXPERIMENTS

Organic	Molecular weight	Density at 20°C (g cm^{-3})	Boiling point (°C)	Vapor pressure at 25°C (mm Hg)	Solubility parameters[a] (δ_o)	(δ_d)	(δ_p)	(δ_h)	Solubility in water (mg L^{-1})[b]
Aliphatic hydrocarbon									
n-Octane	114.23	0.703	125.7	16.71	7.6	7.6	0.0	0.0	6.6
Aromatic hydrocarbons									
Benzene	78.11	0.879	80.1	96.43	9.2	9.0	0.0	1.0	1,178
Toluene	92.13	0.866	110.6	31.96	8.9	8.8	0.7	1.0	515
o-Xylene	106.16	0.897	144.0	8.22	8.8	8.7	0.5	1.5	175
m-Xylene	106.16	0.868	139.3	9.15	8.6	8.4	0.5	1.2	196
p-Xylene	106.16	0.854	137-138	9.41	8.6	8.4	0.5	0.1	190
Chlorinated hydrocarbons									
1,1,1-Trichlorethane	133.42	1.338	74.1	143.35	8.6	8.3	2.1	1.0	1,320
Trichloroethylene	131.40	1.476	87.2	80.30	9.2	8.8	1.5	2.6	1,100
Oxygenated hydrocarbons									
Propionic acid	74.08	0.993	141.1	6.23	12.4	7.5	5.5	8.4	
Acetone	58.08	0.788	56.5	263.2	9.9	7.6	5.1	3.4	
Methyl ethyl ketone	72.10	0.805	79.6	100.0	9.3	7.8	4.4	2.5	240,000
n-Butyl alcohol	74.12	0.810	117.7	8.50	11.3	7.8	2.8	7.7	74,500
n-Butyric acid[c]	88.11	0.964	162.0	1.00	10.5	7.3	2.0	5.2	

[a] δ_o = Hildebrand solubility parameter; δ_d = dispersive solubility parameter; δ_p = polarity solubility parameter; and δ_h = hydrogen-bonding solubility parameter. Barton (11).
[b] Riddick and Bunger (12).
[c] n-Butyric acid observed in the partitioning experiment was the oxidation product of n-butanol.

D1248 is not being strictly followed by the FML industry and users of FMLs. In this specification, a HDPE polymer has a density greater than or equal to 0.941 g cm^{-3}. The term "HDPE," which is used in most of the technical trade literature relating to geosynthetics, is used loosely to refer to a wide range of polyethylene polymers including those that the ASTM specification would consider medium-density polyethylene.

TABLE 3. SELECTED PROPERTIES OF POLYETHYLENE FMLS USED IN STUDY

Polymer	LLDPE	HDPE
FML number[a]	284	483
Nominal thickness (mil)	30	100
Volatiles (%)	...	0.1
Carbon black content (%)	2.5	2.5
Density at 23°C		
FML (g mL^{-1})	0.924	0.945
Polyethylene[b] (g mL^{-1})	0.913	0.936
Crystallinity (%)	36.3	59
Melting point (°C)	119	121

[a]Matrecon identification number.
[b]Calculated from the density of the FML by correcting for the carbon black content.

DISTRIBUTION OF ORGANICS BETWEEN WATER AND AN FML

In the first set of experiments, samples of an FML were placed in the test liquids to determine the distribution of a selected group of organics between water and an FML. The FML samples that were placed in the test liquids were either previously unexposed or already saturated with an organic. The unexposed samples were placed in saturated aqueous solutions of the respective organic, and the samples saturated with organics were placed in DI water.

Distribution of Organics Between Organic-Saturated Water and a Polyethylene FML

To assess the distribution of dissolved organics between an aqueous solution and an FML, a series of saturated aqueous solutions, each containing a single organic, were prepared with an excess of organics and placed in vapor-tight jars. Since acetone, which was in this series, is miscible with water at all proportions, the aqueous solution was prepared at 250,000 mg of acetone per liter (L) of solution.

A specimen of PE FML (No. 483) was immersed in each jar. At intervals, each immersed specimen was removed and weighed until it reached a maximum value; the concentration of the organic in the FML specimen was calculated and reported in mg of organic per L of solution, i.e. per L of FML. The values used for the concentrations of the organics in the saturated aqueous solutions were obtained from the literature (12). The distribution coefficients, i.e. the ratio of the concentration of the organic in the FML to the concentration in the aqueous

TABLE 4. DISTRIBUTION OF NINE ORGANICS BETWEEN SATURATED AQUEOUS SOLUTIONS AND A HIGH-DENSITY POLYETHYLENE FML (NO. 483)

Organic	Concentration of organic in water[a] (C_{H_2O}) (mg L^{-1})	Time to maximum swelling (days)	Weight increase of HDPE FML specimen (%)	Concentration of organic in swollen FML (C_{FML}) (mg L^{-1})	Distribution coefficient (C_{FML}/C_{H_2O})
Acetone	250,000[b]	>44	0.33	3,210	>0.0123
Methyl ethyl ketone	240,000	>46	0.62	5,900	>0.0246
Trichloroethylene	1,100	43	16.71	144,200	131
1,1,1-Trichloroethane	1,320	52	11.70	103,000	78.2
Benzene	1,180	30	7.22	63,900	54.3
Toluene	515	50	8.05	70,600	137
o-Xylene	175	40	8.42	73,800	422
m-Xylene	196	38	8.19	71,800	366
p-Xylene	190	49	8.43	73,600	387

[a]Values which are the solubilities of the organics in water at room temperature were obtained from Riddick and Bunger (12).
[b]Initial concentration of the acetone-water solution; acetone is miscible with water in all proportions.

solution, were calculated. The results of the analyses and calculations are presented in Table 4.

The time required to reach maximum swelling ranged from 30 days for the specimen immersed in benzene solution to 52 days for the specimen immersed in the TCE solution. The distribution of all of the organics, except the acetone and MEK, was predominantly to the HDPE specimens, and the distribution coefficients ranged from 54 for benzene to 422 for o-xylene. The distribution coefficients for acetone and MEK are low, probably reflecting the limited absorption of those organics by the HDPE FML and their relatively low rates of diffusion in the FML (3, 4). It should be noted that the higher values for the distribution coefficients are for organics that are less polar and have solubility parameters (δ_o, δ_d, δ_p, and δ_h) that closely match those of the polyethylene. The respective values for a polyethylene of approximately the same density as FML (No. 483) are 7.93, 8.05, 0.05, and 0.98 (13).

Distribution of Organics Between a Saturated Polyethylene FML and Deionized Water

In this experiment, individual specimens of the same polyethylene FML (No. 483) were saturated with each of the organics. These specimens, approximately 1 x 3 in. in size and 2 g in weight, were initially immersed in the respective organics and weighed daily until equilibrium was reached. Once the specimens were saturated, they were immersed in vapor-tight jars filled with DI water. The vapor-tight jars consisted of 8-oz glass jars with ground and polished-top edges, and Teflon-lined phenolic resin tops, each of which was

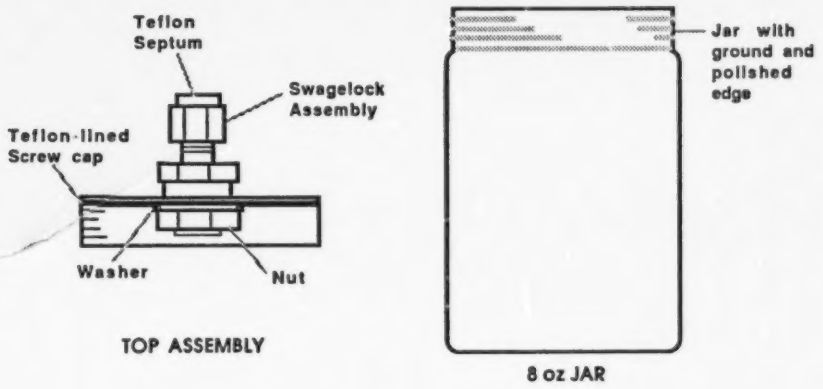

FIGURE 1. Schematic of the Immersion Test Jar

fitted with a Swagelock sampling port and Teflon-lined silicone rubber septums for withdrawing samples of water for GC analysis (Figure 1). The water in each jar was sampled periodically and analyzed by GC (Set of Conditions 1 described in Table 1) for the organic that transferred from the saturated FML specimen. The water was sampled with a 1-μL syringe initially at 5-min. intervals and then hourly until the concentration of the organic in the water had plateaued, at which time the specimen was withdrawn and weighed. The concentration of the organic remaining in the FML specimen was determined by HSGC.

Data on the weight at maximum swelling of the specimens at saturation as well as the weights of the swollen specimens after equilibrating with the water in the jars, and the time required for each to reach equilibrium are presented in Table 5. The rates at which the absorbed organics diffused out of the FML into the water varied considerably. It took 24 hours for the water containing the specimen swollen with TCE to reach equilibrium concentration, whereas the water containing the specimen swollen with benzene required 120 hours.

The distribution coefficients, which are also presented in Table 5, show the strong tendency of the chlorinated and aromatic organics to remain in the polyethylene FML (No. 483). It does not appear that equilibrium had been reached with acetone and MEK when the specimens were withdrawn after 120 hours, probably due to the low permeability and diffusion of these organics in polyethylene (3, 4). Consequently, the concentrations of these organics in the FML at 120 hours were high and those in the water were low, resulting in high apparent values for the distribution coefficients.

DISTRIBUTION OF ORGANICS IN A TEST APPARATUS CONSISTING OF THREE COMPARTMENTS SEPARATED BY POLYETHYLENE FMLS

Three-Compartment Test Apparatus

In order to assess the permeation of organics from a dilute aqueous solution through polymeric FMLs under conditions that simulate service conditions for an FML, a three-compartment closed apparatus was fabricated (13) The test apparatus, shown schematically in Figure 2, can be divided into seven zones, which are listed in Table 6. The inside diameter of the compartment was 4 inches. FML specimens separate the three compartments (Zones 2 and 5). An aqueous solution containing organics partially fills the middle compartment (Zone 4), and DI water can be placed in the bottom compartment (Zone 7). Once the test apparatus is assembled, the organics can either volatilize into the

TABLE 5. DISTRIBUTION OF ORGANICS BETWEEN AN ORGANIC-SATURATED HIGH-DENSITY POLYETHYLENE FML (NO. 483) AND DEIONIZED WATER

Organic	Saturated FML		At equilibrium in deionized water				
	Maximum swelling, by weight (%)	Concentration of organic (mg L^{-1})	Time to maximum concentration in H_2O (hours)	Swelling of FML, by weight (%)	Concentration of organic in FML (C_{FML}) (mg L^{-1})	Concentration of organic in water (C_{H_2O}) (mg L^{-1})	Distribution coefficient (C_{FML}/C_{H_2O})
Acetone	0.96	9,080	>120[a]	0.62	5,830	35[a]	<167
Methyl ethyl ketone	1.83	17,120	>120[a]	0.91	8,990	127[a]	<71
Trichloroethylene	17.52	150,500	24	8.98	84,800	966	88
1,1,1-Trichloroethane	12.13	106,700	50	6.91	65,800	589	112
Benzene	7.61	67,100	120	1.95	19,030	643	30
Toluene	8.40	73,400	46	4.42	42,000	266	158
o-Xylene	8.73	76,300	52	7.07	65,600	186	352
m-Xylene	8.51	74,300	78	6.70	62,200	193	322
p-Xylene	8.72	75,900	58	6.93	64,300	165	390

[a]Equilibrium did not appear to have been reached when specimen was removed from test at 120 hours.

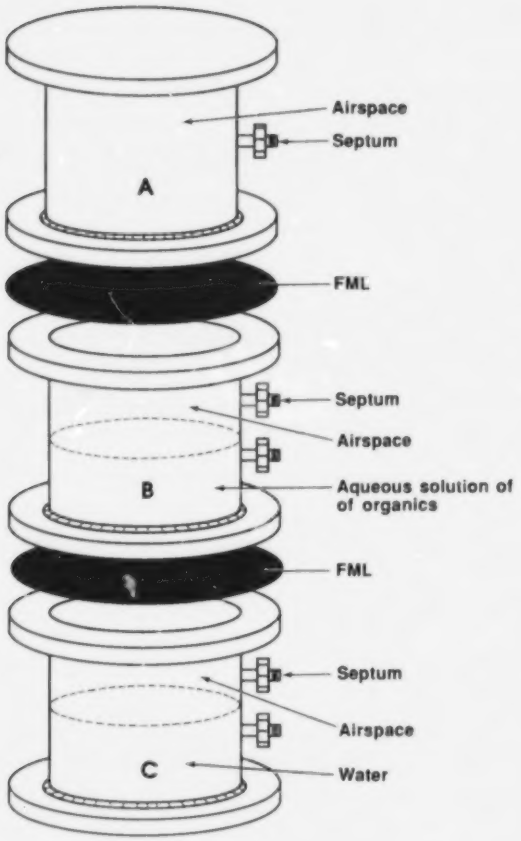

FIGURE 2. Schematic of the Three-Compartment Test Apparatus

airspace above the solution and then, permeating through the top FML specimen, enter the top compartment or the organics can permeate through the lower FML specimen and into the bottom compartment.

To prevent the loss of volatiles, the covers of one end of each of the top and the bottom compartments were welded to the walls. The three compartments were clamped tightly together using clamps that fit around the outside edges of the flanges and are tightened by bolts. The apparatus was assembled with a Teflon tape, such as that used with threaded pipe fittings, as a seal between the different compartments.

Ports with Teflon silicone rubber septums were incorporated in each of the three compartments for use in withdrawing samples for GC analysis from the aqueous and airspace zones. Thus, two FML zones could be analyzed by HSGC after the apparatus was dismantled.

The three-compartment apparatus simulates the configuration of a covered landfill as follows:

- o The airspace in the top compartment simulates the airspace over a "cover" liner. The FML specimen between the top and middle compartments simulates a "cover" liner.
- o The airspace in the middle compartment simulates the headspace above a waste liquid, and the dilute solution containing or-

TABLE 6. ZONES IN THREE-COMPARTMENT TEST APPARATUS

Zone	Compartment	Description	Volume (mL)
1	Top	Airspace above "cover"	806
2	Barrier between top and middle	"Cover" FML (33-mil LLDPE): Area exposed to solution	~7
3	Middle	Airspace above aqueous solution containing organics	306
4	Middle	Dilute aqueous solution containing organics	500
5	Barrier between middle and bottom	"Bottom liner" (33-mil LLDPE): Area exposed to solution	~7
6	Bottom	Airspace below "bottom liner" FML	506
7	Bottom	Deionized water	300
		Total	2,432

ganics serves as the waste liquid. The FML specimen between the middle and bottom compartments simulates the service conditions of a single bottom liner.

- The airspace and the deionized water in the bottom compartment simulate, respectively, pore space in the soil and the groundwater.

The configuration of the zones within each compartment can be modified to assess double liners and various auxiliary materials, such as soil covers, geotextiles, and drainage materials.

Distribution of Two Organics in Test Apparatus

In the first experiment of this series, toluene and TCE were simultaneously dissolved in the water in the middle compartment at concentrations less than saturation. Both of these organics are commonly found in leachates and are easily identifiable and trackable by GC analysis. A LLDPE FML (No. 284) separated the three compartments.

In this experiment, Zone 4 was filled with 500 mL DI water and spiked with 191 mg each of toluene and TCE to yield concentrations of 382 mg each per L of water. The five zones containing water or vapor were sampled and analyzed by GC (Set of Conditions 2 described in Table 1) periodically to assess the changes in concentrations in these zones. After 256 hours, when the concentrations appeared to have reached equilibrium, the apparatus was dismantled and the FML samples were removed and analyzed by HSGC to determine the concentrations of the organics in the FMLs. The results of analyzing the samples taken at 24, 96, and 256 hours are reported in Table 7.

TCE was detected in all zones of the apparatus that were sampled within 24 hours after exposure began. Toluene was detected in all zones, except the groundwater (Zone 7), within 24 hours, and appeared in the groundwater by 96 hours. After 256 hours of test, the relative concentrations of the two organics were the same in both aqueous zones (Zones 4 and 7), and were similar in the three airspace zones (Zones 1, 3, and 6), indicating that the apparatus was

TABLE 7. DISTRIBUTION OF TRICHLOROETHYLENE (TCE) AND TOLUENE IN THREE-COMPARTMENT TEST APPARATUS SEPARATED BY A LINEAR LOW-DENSITY POLYETHYLENE FML (NO. 284)

Zone				Start of test		At 24 hours		At 96 hours		End of test at 256 hours	
No.	Description	Volume (mL)	Organic	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})
1	Airspace above "cover" FML	806	TCE	0	0	9.2	11.5	14.1	17.5	12.9	16.0
			Toluene	0	0	7.9	9.8	10.0	12.5	4.8	6.0
2	"Cover" polyethylene FML	7.02	TCE	0	0	...	...	...	...	56.1	7,990
			Toluene	0	0	...	...	...	...	60.2	8,570
3	Airspace above test liquid	306	TCE	0	0	12.1	39.5	8.8	29.0	5.97	19.5
			Toluene	0	0	10.1	33.0	8.1	26.5	1.83	6.0
4	Test liquid	500	TCE	191	381	95	190	80	160	22.5	45.0
			Toluene	191	381	92	185	80	160	35.7	71.4
	Barrier FML	7.02	TCE	0	...	...	...	...	...	56.1	7,990
			Toluene	0	...	...	...	...	...	60.2	8,570
6	Airspace below FML	506	TCE	0	...	8.6	17.2	11.9	23.5	9.87	19.5
			Toluene	0	...	1.16	2.3	3.74	7.4	2.58	5.1
7	"Groundwater"	300	TCE	0	...	0.75	1.5	6.42	21.4	13.5	45.0
			Toluene	0	...	0	0	4.57	15.2	21.4	71.4
	Total	2,432	TCE	191	381	125.6	...	121	...	176.9	...
			Toluene	191	381	111.1	...	106.4	...	186.7	...
	Fraction accounted for, %		TCE	100		65		63		92.6	
			Toluene	100		58		55		97.7	

dismantled to allow analysis of the FML specimens. The data show that the concentrations in the airspaces (Zones 1, 3, and 6) were similar in value and the concentrations in the two FML specimens were essentially equal. Overall, 92.6% of the TCE and 97.7% of the toluene were accounted for in the final analyses of all zones. The HSGC analysis of the FML in the flange area showed no organics, which indicated that there was no leakage through the flanges. Overall, these results show that the apparatus had come to equilibrium; they also show the high absorption of the two organics by the FML. At these equilibrium conditions, the distribution coefficients between the LLDPE FML and water for TCE and toluene were 178 and 120, respectively.

Distribution of Six Organics in Test Apparatus

In another experiment performed with the same type of test apparatus, same configuration of zones, and same polyethylene FML (No. 284), 191 mg each of six organics were injected into the 500 mL of water in the middle compartment in Zone 4; the organics included n-octane, TCE, toluene, o-xylene, n-butanol, and propionic acid. Table 2 presents data on these organics. Due to the low solubility of n-octane in water, the amount of this organic added to the water was excessive.

The five zones that contained either liquid or vapor were monitored by sampling and analysis by GC. Exposure in the test apparatus was continued until essentially no change took place in the concentrations of these chemicals in any given zone. At 28 days, the analyses indicated that concentrations of the toluene and TCE had reached equilibrium, at which time the test apparatus was dismantled and the FMLs were analyzed by HSGC for the organics that they had absorbed (Set of Conditons 3 described in Table 1). The results, which include concentration data for 24 hours, 96 hours, and 28 days, are presented in Table 8.

As in the previous experiment, TCE was found in all zones within 24 hours after exposure. Toluene and n-octane were found in all zones within 96 hours, while o-xylene appeared in all zones but the "groundwater" zone in the 28-day samples. Propionic acid moved only into the "groundwater" zone (Zone 7). Seventy-five to 85% of the aliphatic, aromatic, and chlorinated hydrocarbons, and 57% of the propionic acid were accounted for in the final analyses. The n-butanol, which was injected into Zone 4 at the beginning of the test, was not detected after about a week and appeared to be replaced by n-butyric acid which was detected by GC analysis. Based on a total conversion of n-butanol to n-butyric acid, 11.5% of the n-butanol was accounted for as n-butyric acid in the final analyses. A portion of the apparent loss of the organics can probably be attributed to the large number of samples withdrawn from the test apparatus during the 28 days of exposure for GC analysis to track the organics.

The distribution and transport of each of the organics that were initially placed in the water in Zone 4 are discussed briefly in the following subsections.

n-Octane. The n-octane was injected at a concentration substantially above its solubility in water. It appeared within 24 hours in the airspace above the spiked water and was substantially absorbed by the upper FML. In the final analysis, essentially 75% of the spike was concentrated in the upper FML, a small amount was detected in the lower FML, and the remainder was observed in the airspaces, particularly in the upper airspace (Zone 1). Only a trace amount was found in the liquid in the bottom compartment.

Only limited amounts of n-octane migrated downwards into the lower FML and into the airspace below the FML because of its low solubility in water and its low density, which caused it to form a free phase that floated on the water. The absorption of the n-octane by the upper FML is attributed to its solubility in the FML, both of which have essentially the same solubility parameter value.

Trichloroethylene. The spike of the trichloroethylene (TCE) was approximately 1/3 of the solubility of TCE in water. Due to its volatility, the TCE was observed quickly in the space above the spiked water in Zone 4 and also in

the airspace above the upper FML. In the final analysis, the TCE was present in all zones, although approximately 50% of that measured was in the FMLs; a substantial amount was transported into the liquid in the bottom compartment, i.e. the "groundwater" zone.

These results show the tendency of the TCE to migrate and to be transported through all phases and reflect the solubility of TCE in water as well as in FMLs. At the end of the test, of the six organics in the study, the TCE had the highest concentration in the water in the bottom compartment. The results indicate that special efforts are needed to control this organic.

Toluene. The amount of toluene injected into the water in Zone 4 was below its solubility level in water. Toluene behaved similarly to the TCE, although it did not migrate as rapidly. However, it was in the airspace above the upper FML in essentially the same concentration as the TCE. As with the TCE, only a small quantity of the toluene was present (0.3 mg) below the lower FML at the end of 24 hours.

At the time of dismantling, the toluene was present in all seven zones, with approximately 77% of the total in the two FML layers. As with the TCE, it moved through all zones of the test apparatus. The results indicate that special efforts are needed to control this organic.

o-Xylene. The amount of o-xylene injected into the water in Zone 4 was approximately twice its solubility level in water, i.e. 382 vs. 175 mg L^{-1}, and it was anticipated that the o-xylene would tend to migrate relatively rapidly. The o-xylene appeared to have left Zone 4 quickly; it was detected at significant concentrations (up to 13 mg L^{-1}) in the airspaces after 24 hours; only a trace was detected in the water in Zone 4, and none in the water in the bottom compartment.

In the final analyses, the o-xylene was concentrated principally in the FMLs; almost all of it had migrated out of the spiked water. Also, the concentration in the airspaces was low in comparison with that in the FMLs, which demonstrates the strong affinity of the o-xylene for the FML and reflects its comparatively low solubility in water.

Propionic Acid. Propionic acid has a high solubility parameter value and is completely miscible with water; therefore, it has a strong affinity for water. Only 57% of the propionic acid that was injected at the beginning of the experiment was accounted for in the final analyses; approximately 75% of that was still in the spiked water and the remainder was detected in the water in the bottom compartment. No propionic acid was detected in the other zones of the test apparatus.

n-Butanol. After the first few days of analyses, no n-butanol was observed in any of the zones. However, n-butyric acid appeared in the analyses, indicating that the n-butanol had been oxidized to n-butyric acid. No butyl propionate appeared in the GC scan; thus, the possibility of esterification of the n-butanol with the propionic acid could be discounted. Assuming that the n-butanol was completely converted to n-butyric acid, 11.5% would have been accounted for as n-butyric acid which was detected only in the aqueous phases.

During the dismantling of the test apparatus, there was considerable pressure in the bottom compartment, which may have been CO_2 generated from the decomposition of the acids. However, CO_2 cannot be detected by flame-ionization detection in the GC. It was also noted that the bottom compartment fabricated of aluminum exhibited some corrosion and darkening of the surface. No explanation is offered for the cause of the corrosion or for the effects on the experiment.

DISCUSSION

The experiments on the distribution of volatile organics from dilute aqueous solutions show that, even at low concentrations, some organics can be

TABLE 8. DISTRIBUTION OF ORGANICS FROM A DILUTE AQUEOUS SOLUTION OF SIX ORGANICS IN TEST APPARATUS CONSISTING OF THREE-COMPARTMENTS SEPARATED BY POLYETHYLENE FML (NO. 284) BARRIERS

Zone				Start of test		At 24 hours		At 96 hours		End of test at 28 days	
No.	Description	Volume (mL)	Organic	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})
1	Airspace above "upper" FML	806	n-Octane	0	0	12.1	15	4.8	6	2.58	3.2
			Trichloroethylene	0	0	8.1	10	12.5	15.5	19.3	24.0
			Toluene	0	0	28.3	35.1	8.1	10.0	5.64	7.0
			o-Xylene	0	0	10.7	13.3	4.8	6	4.19	5.2
			Propionic acid	0	0	-----none----		----none-----		------none-----	
			n-Butanol	0	0	-----none----		----none-----		------none-----	
2	"Upper" polyethylene FML	7.02	n-Octane	0	0	analyzed by headspace GC when the apparatus was dismantled				126.7	18,051
			Trichloroethylene	0	0					37.8	5,885
			Toluene	0	0					49.3	7,024
			o-Xylene	0	0					76.0	10,829
			Propionic acid	0	0					------none----	
			n-Butanol	0	0					------none----	
3	Airspace above spiked water	306	n-Octane	0	0	20.8	68.0	18.7	61	0.98	3.2
			Trichloroethylene	0	0	12.2	40	4.90	16	6.23	20.1
			Toluene	0	0	11.3	37	3.21	10.5	2.14	7.0
			o-Xylene	0	0	2.1	6.8	1.04	3.4	1.59	5.2
			Propionic acid	0	0	-----none----		-----none-----		-----none-----	
			n-Butanol	0	0	-----none----		-----none-----		-----none-----	
4	Spiked water	500	n-Octane	191	382	0.3	0.6	0.3	0.6	0.3	0.6
			Trichloroethylene	191	382	40.1	80	20.0	40	17.1	34.2
			Toluene	191	382	48.1	96	22.5	45	15.0	30.0
			o-Xylene	191	382	----trace----		----trace-----		0.5	1
			Propionic acid	191	382	106	212	102	204	99.7	199.5
			n-Butanol	191	382	140	280	110	220	-----none-----	
			n-Butyric acid[a]	0	0	-----none----		----trace-----		20.75	41.25

5	"Lower" polyethylene FML	7.02	n-Octane	0	0	analyzed by headspace GC when the apparatus was dismantled				2.60	370
			Trichloroethylene	0	0					47.60	6,780
			Toluene	0	0					61.15	8,712
			o-Xylene	0	0					76.04	10,833
			Propionic acid	0	0					------none-----	
			n-Butanol	0	0					------none-----	
6	Airspace below "lower" FML	506	n-Octane	0	0	-----none----		1.36	2.7	1.29	2.56
			Trichloroethylene	0	0	0.4	0.8	2.6	5.2	14.2	28.2
			Toluene	0	0	0.3	0.6	3.8	6.5	5.0	10.0
			o-Xylene	0	0	0.03	0.015	0.126	0.25	1.9	3.75
			Propionic acid	0	0	-----none----		-----none-----		------none-----	
			n-Butanol	0	0	-----none----		-----none-----		------none-----	
7	Bottom water	300	n-Octane	0	0	-----none----		----trace-----		-----trace-----	
			Trichloroethylene	0	0	0.15	0.5	4.23	14.1	20.58	68.6
			Toluene	0	0	-----none----		0.468	1.56	5.6	18.75
			o-Xylene	0	0	-----none----		-----none-----		-----none------	
			Propionic acid	0	0	-----none----		----trace-----		10.1	33.15
			n-Butanol	0	0	-----none----		-----none-----		-----none------	
			n-Butyric acid[a]	0	0	-----none----		----trace-----		5.4	18.0

		Total in all zones[b]	
n-Octane	191	155.03	(81.0)
Trichloroethylene	191	162.8	(85.2)
Toluene	191	143.8	(75.3)
o-Xylene	191	160.2	(83.9)
Propionic acid	191	109.8	(57.4)
n-Butanol	191	0	(0)
n-Butyric acid[a]	0	26.15	(11.5)

[a]n-Butanol appeared to have been oxidized to n-butyric acid which was detected in the GC as the amount of n-butanol detected in the closed apparatus decreased.
[b]Data in parentheses are the percent of initial organics accounted for in the final analysis.

TABLE 9. COMPARISON OF THE SWELLING OF A HIGH-DENSITY POLYETHYLENE FML[a] (NO. 483) IMMERSED IN NEAT ORGANICS AND IN SATURATED AQUEOUS SOLUTIONS OF ORGANICS

Organic	Neat organic		Saturated aqueous solution	
	Maximum swelling, by weight (%)	Time to maximum swelling (days)	Maximum swelling, by weight (%)	Time to maximum swelling (days)
Acetone[a]	0.96[b]	>18	0.33[b]	>44
Methyl ethyl ketone	1.83[b]	>21	0.62[b]	>46
1,1,1-Trichloroethane	12.13	17	11.70	52
Trichloroethylene	17.52	15	16.71	43
Benzene	7.61	6	7.22	30
Toluene	8.40	6	8.05	50
o-Xylene	8.73	9	8.42	40
m-Xylene	8.51	6	8.19	38
p-Xylene	8.72	7	8.43	49

[a]Acetone is miscible with water in all proportions; the concentration was set at 250,000 mg L^{-1} for the experiment with the aqueous solution.

[b]Swelling probably had not come to equilibrium.

highly absorbed by a polymeric FML immersed and can rapidly permeate the liner. Table 9 compares the swelling of an HDPE FML immersed in a series of neat organics with the swelling of the same FML immersed in a series of saturated aqueous solutions of the same organics. These results show that the amount of organic an FML can absorb during exposure to an aqueous solution of an organic maintained at saturation concentration can approach the amount the FML can absorb during direct exposure to the neat organic. The aqueous solutions were maintained at saturation concentration by preparing the solutions with an excess of the organics, i.e. by adding more of each organic than is soluble in water at room temperature; thus, each solution was always in contact with a neat organic. Even though the maximum swelling values for the specimens exposed to the neat organics were all somewhat higher, the maximum swelling values obtained by direct immersion in the neat organics were approximately equal to those obtained by immersion in the saturated dilute solutions. Based on permeability data (3, 4), it appears that the swelling had not come to equilibrium in acetone and MEK, and in the saturated solutions of these organics.

The results presented in Table 9 also show that the time to reach maximum swelling values can be significantly affected by the concentration of the organic in the liquid in contact with the FML. The specimens exposed to the neat organics reached maximum swelling values in considerably shorter times than the specimens exposed to the saturated aqueous solutions.

The results of determining the distribution of organics between saturated FML specimens and DI water indicate that the concentration of an organic in an in-service FML is affected by the concentration of the organic in the liquid in direct contact with the FML and that the concentration of the organic in the FML will change as the concentration of the organic in the liquid in contact with the FML changes.

The results of measuring the distribution of organics in the different zones of a multi-compartment apparatus indicate that the amount and rate of absorption and the transport of these species through a polymeric FML is a function of such factors as relative solubility parameters of the FML and the organic, crystallinity of the FML, and molecular weight and concentration of the organic constituent. A multi-compartment apparatus, such as the one described and used in this work, appears to be an appropriate and promising means of

assessing the effectiveness of an FML to contain the organic constituents of a given leachate.

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